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Atom Trap Trace Analysis of Calcium Isotopes

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2005

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Hoekstra, S. (2005). *Atom Trap Trace Analysis of Calcium Isotopes*. s.n.

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Chapter 1

Introduction

1.1 Isotope abundances

In 1919 Aston discovered [1] that the atomic mass of neon is not 20.20, but that neon consists of a mixture of two isotopes with different abundances and integer mass: ^{20}Ne and ^{22}Ne with a ratio of 10:1. Since then it became known that all elements can come as isotopes, with varying abundances and stability¹. Chemically the different isotopes of an element behave the same, and that is why physics techniques are needed to make a distinction between the isotopes. Knowledge on the abundance ratio between two isotopes has important applications in various fields.

An example of the use of the ratio between two stable isotopes is the $^{18}\text{O}/^{16}\text{O}$ ratio. This ratio has been used to reconstruct the history of the temperature fluctuations of the earth [2]. Small air bubbles in the ice at the polar regions captured the air from the period in which the ice was deposited. Since the $^{18}\text{O}/^{16}\text{O}$ oxygen isotope ratio is sensitive to the temperature, the periods of the ice-ages could be reconstructed from an analysis of the air in these bubbles. Both isotopes of oxygen are stable, and the ratio in abundance is roughly 1:50. Very precise measurements of the small deviations of this ratio are used to extract information on the temperature history.

The challenge in the measurement of rare unstable isotopes is quite different. The relative abundance of these rare isotopes is in the range of 10^{-10} to 10^{-16} . The abundance ratio changes over a much wider range, so instead of a precision measurement here the focus is more on just detecting the rare isotope.

The most well known example of the use of unstable isotopes is the ^{14}C dating method, which is based on the $^{12}\text{C}/^{14}\text{C}$ ratio ([3] and references therein). In the atmosphere this ratio is constant, but in a tree this ratio changes with time when the tree dies and it no longer absorbs ^{14}C from the atmosphere. The ratio changes because the ^{14}C nuclei decay, with a half-life of 5730 years. The accurate determination of this isotope ratio has

¹Now we know that neon occurs as three stable isotopes ^{20}Ne (90.48 %), ^{21}Ne (0.27 %) and ^{22}Ne (9.25 %) with an average mass number of 20.18

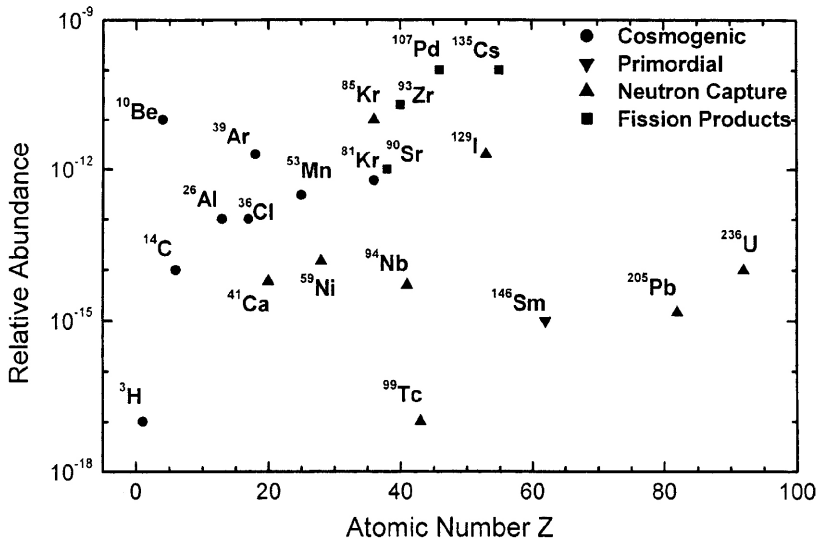


Figure 1.1: The major isotopes with a relative abundance below 10^{-10} . Figure adapted from Wendt et al [7]

become an extremely valuable method to date various materials containing carbon of 500 to 50,000 years old. These are just two examples: a large range of applications has been found based on the ratio of isotopical abundances. Trace analysis of long-lived radioactive isotopes has become an important tool in a wide variety of fields. Ranging from medical science to environmental research, from nuclear safety to archeology, the capability to detect low-abundance long-lived isotopes has opened many research fields [4–6].

These advances are an important incentive to push the detection limit further, and be able to detect isotopes with even smaller abundances. With the rapid development in the last decades of high-power narrow-band lasers the development of new methods for isotope separation and detection have become possible.

In figure 1.1 the major isotopes with relative abundance less than 10^{-10} are shown, including their origin. Most of these very rare isotopes are long-lived with lifetimes ranging from a few thousand to millions of years. These long-lived radionuclides can originate either from natural or human sources. The radionuclides of natural origin are produced in a number of ways: in the nucleosynthesis process in stars, as a decay product of uranium or thorium, by cosmic-ray induced reactions in the atmosphere or through natural fission. The man-made radioactive nuclides find their origin in human activities such as nuclear industry, bomb tests, medical applications, etc.

In this thesis we report on the development of a new method for the ultra-sensitive detection of rare isotopes, based on the laser cooling and trapping of neutral atoms. The specific isotope we are interested in is ⁴¹Ca. This isotope of calcium exists in nature at

Table 1.1: Properties of the calcium isotopes. Shown are the relative natural abundance and the half-life time

<i>Isotope</i>	<i>Rel. nat. abundance</i>	<i>Half-life</i>
39	-	859.6 ms
40	0.9694	stable
41	$1 \cdot 10^{-14}$	104,000 yrs
42	0.0065	stable
43	0.0014	stable
44	0.0209	stable
45	-	162.61 d
46	0.00004	stable
47	-	4.536 d
48	0.0019	$6 \cdot 10^{18}$ yrs
49	-	8.718 m

a natural abundance which is 14 orders of magnitude lower than that of all the calcium isotopes together. Why should we be interested specifically in ^{41}Ca ? In the following it will be shown that ^{41}Ca can provide key understanding on bone diseases and that it could be used as a dating isotope complementary to ^{14}C dating.

1.2 Why ^{41}Ca ?

^{41}Ca is an extraordinary isotope of calcium. Two unique properties make ^{41}Ca suitable for a range of possible applications, as will be explained in this section. The first property is the low abundance of 10^{-14} with respect to ^{40}Ca , which makes up 97 % of all calcium occurring in nature. This low abundance makes that ^{41}Ca is the most attractive calcium isotope to be used as a tracer in biomedical research, as will be explained in section 1.2.3. The second property is the instability of ^{41}Ca : a ^{41}Ca atom decays on average 100,000 years after it was produced. It is this long lifetime that makes ^{41}Ca a candidate for the development of radiocalcium dating, as will be explained in section 1.2.4. In table 1.1 the half-life time and the abundance of ^{41}Ca are compared with the other calcium isotopes. The long lifetime and the low abundance of ^{41}Ca can be understood from the origin and the decay of ^{41}Ca .

1.2.1 The origin and decay of ^{41}Ca

In figure 1.2 it is illustrated how ^{41}Ca is produced in the atmosphere. ^{41}Ca is a long-lived cosmogenic nucleus, which means that it is (in)directly produced by cosmic ray particles and that the nucleus is not completely stable. The half-life of ^{41}Ca is estimated at $1.04 \pm 0.05 \cdot 10^5$ years [8]. In the direct process ^{41}Ca is created via the spallation of

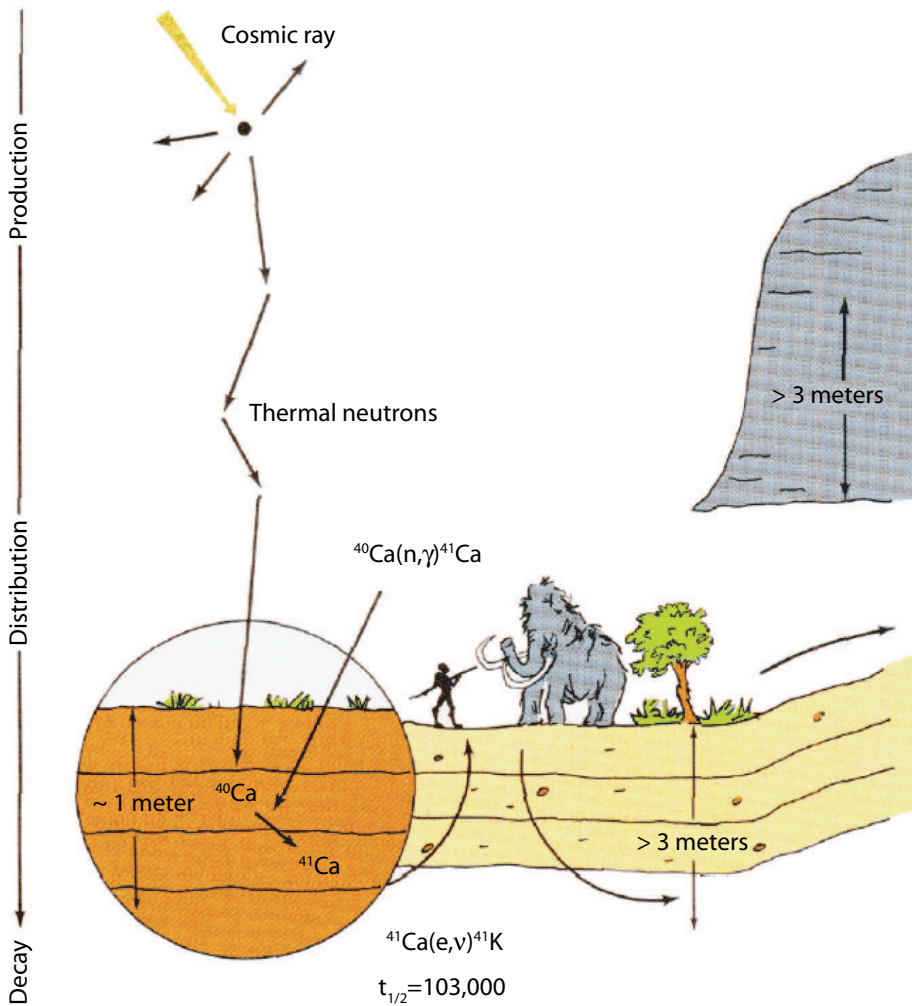


Figure 1.2: An illustration of how ^{41}Ca is produced and decays. The low abundance makes it suitable as a biomedical tracer, the long lifetime for radiocalcium dating. Shown here is how bone material has to be shielded from thermal neutrons to stop the production of ^{41}Ca for the dating application to be reliable. Adapted from Taylor [9]

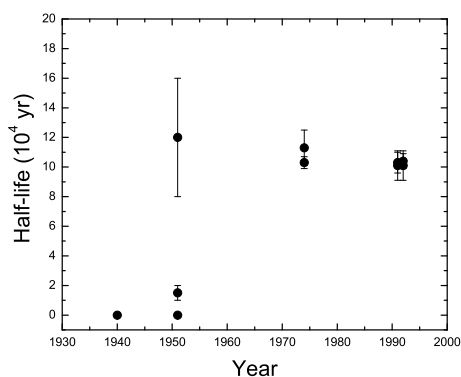


Figure 1.3: The half-life of ^{41}Ca over the years

year	value (yr)	ref.
1935	-	[18]
1939	-	[19]
1940	0.023 ± 0.0022	[20]
1947	< 1 day	[21]
1951	0.246 ± 0.082	[13]
1951	$15,000 \pm 5,000$	[14]
1951	$120,000 \pm 40,000$	[14]
1972	$130,000 \pm 10,000$	[22]
1974	$103,000 \pm 4,000$	[15]
1974	$113,000 \pm 12,000$	[15]
1991	$103,000 \pm 7,000$	[16]
1991	$101,000 \pm 10,000$	[17]
1992	$101,000 \pm 10,000$	[23]
1992	$104,000 \pm 5,000$	[8]

Table 1.2: Reported values of the half-life of ^{41}Ca

following the pre-enrichment of ^{41}Ca at the Oak Ridge National Laboratory using a Calutron isotope separator. The value obtained was $2.0 \pm 0.5 \cdot 10^{-14}$ [26] for the $^{41}\text{Ca}/\text{Ca}$ ratio in contemporary bovine bone.

1.2.3 Biomedical research

Perhaps the most promising applications of ^{41}Ca are in the field of biomedical research. Calcium is an important element in the human body: it is a major constituent of the bone structure, and in the form of Ca^{2+} plays an important role on the cellular level as a messenger ion. The low natural abundance of ^{41}Ca combined with the low radioactivity of the isotope make ^{41}Ca ideal as a tracer.

The required detection sensitivity ranges from 10^{-8} to 10^{-12} , which is within the range of various experimental methods (Accelerator Mass Spectrometry (AMS), Resonance Ionization Mass Spectroscopy (RIMS) and Atom Trap Trace Analysis (ATTA)). These techniques will be briefly introduced in section 1.3.

Osteoporosis and related bone research

Calcium isotopes other than the main isotope ^{40}Ca can be used as tracers for studying calcium metabolism in living systems. The most relevant information about bone health is transfer of calcium into and out of the bone. During growth this balance is positive, resulting in an increase in bone mass until a peak value is reached in the third decade in life [27]. From then onwards the balance becomes increasingly negative, resulting in a reduction of the bone mineral density. When the reduction of bone mineral density is progressive, osteoporosis develops. This is associated with an increased risk in hip and spine fractures. Apart from reducing the quality of life, the financial costs of osteoporosis are enormous. In 1996, for example, total direct hospital costs arising from hip fractures

alone amounted nearly €4 billion within the European Union [28].

Because calcium turnover in bone is so slow, bone calcium can, in principle, be labelled in-vivo by administering calcium isotopes. When all of the label isotope that has not been incorporated into the bone matrix has been excreted from the body, any label isotope recovered in the urine originates from the bone. Such a direct signal from the bone could be used for direct identification of changes in the bone calcium balance.

Although technically possible, the use of the stable isotopes ^{42}Ca and ^{44}Ca [29] is practically impossible due to the outrageous costs of labelling the skeleton in-vivo [28]. The use of the short-lived radionuclides ^{45}Ca (165 d) and ^{47}Ca (45 d) is not a real option because of the damage done to the human body due to energy release associated with their radioactivity. This does however not hold for the long-living radionuclide ^{41}Ca . This opens up the possibility of labelling bone Calcium in-vivo with negligible health risk, provided that ultra-sensitive techniques for ^{41}Ca analysis are available. The technique of ^{41}Ca trace analysis might not only open up new perspectives for intervention in man, it could, in principle, be used for patients at risk of developing osteoporosis by labelling them with ^{41}Ca .

Because of the low radioactivity $^{41}\text{Ca}/\text{Ca}$ fractions of up to 10^{-8} can be used. After initial elimination of tracer ^{41}Ca from the calcium pools subsequent skeletal calcium turnover maintains and modulates the urine ^{41}Ca content. If in response to a given treatment the rate of bone resorption increases then this can be seen by a decrease of the $^{41}\text{Ca}/\text{Ca}$ ratio in the urine [30].

Many people have already been administered ^{41}Ca as a side-effect of the use of ^{45}Ca and ^{47}Ca . Until recently, it was not known that ^{45}Ca and ^{47}Ca preparations also contain ^{41}Ca . The ^{41}Ca level depends on the proportion of ^{40}Ca in the enriched ^{44}Ca or ^{46}Ca , the period of neutron activation, and the time between irradiation and usage [30,31].

It should be mentioned that also from nutrition research there is much interest in sensitive methods to detect ^{41}Ca . Stable isotope techniques and radioisotope methods are the only reliable tools available for determination of the absorption, retention, or utilization of a nutrient by the human body [27]. The progress in this field of research depends mainly on improving existing stable isotope techniques and on developing novel concepts. By improving precision in isotope analysis, isotope doses in experiments on man can be reduced to physiologically more meaningful levels. This will also enable reduction of the (often substantial) costs of isotopically labelling a nutrient in a test meal. Improvements in the mass spectrometric sensitivity will enable the development of new tracer techniques that have the potential to provide the information required by:

1. governmental institutions for designing food fortification programs;
2. the food industry for developing nutrient-fortified food products; and
3. public health authorities for establishing reliable dietary recommendations for intake of inorganic nutrients.

The effect of carcinogenic substances on cell messengers

As a kind of cell messenger, Ca^{2+} in cytoplasm of human cells plays an important role in maintaining many normal functions of cells. However, the level of Ca^{2+} in cells

increases when the cells are exposed to carcinogenic substances. The problem is where does the increased Ca^{2+} comes from? There are three possibilities: (1) from the outside of the cytoplasm membrane, (2) from the inside of the nucleus or organelles and (3) from both the outside and the inside of the cells. A collaboration has been set up to investigate this problem using cells which have been labelled with ^{41}Ca , planning to do the measurements with AMS [32].

A neutron specific biomarker in tooth enamel

The measurement of long-lived radionuclides, produced by neutrons originating from the nuclear-bomb explosions, offers the possibility to reconstruct neutron fluences to which survivors in Hiroshima and Nagasaki were exposed. ^{41}Ca is suggested here as a means for a retrospective determination of thermal neutron fluences, directly within the human body of a survivor. As proper material tooth enamel is proposed. The ^{41}Ca signal in tooth enamel may be correlated with the exposure to thermal neutron fluences from the nuclear bomb explosions, provided the natural background level of $^{41}\text{Ca}/\text{Ca}$ is significantly lower. Therefore, tooth samples of survivors which were not exposed by the radiation resulting from the explosions have been examined by means of AMS, in order to quantify the natural background level of $^{41}\text{Ca}/\text{Ca}$. Measured $^{41}\text{Ca}/\text{Ca}$ ratios were found to be as low as about $2 \cdot 10^{-15}$. Thus, the bomb induced additional signal should be detectable for survivors at epidemiological relevant distances. Since tooth enamel had already been used as a dosimeter for gamma radiation from the nuclear bomb explosion, the detection of ^{41}Ca in tooth enamel would allow, for the first time, an assessment of both, γ -ray and neutron exposures in the same biological material [33].

1.2.4 Radiocalcium dating

Already in 1963 it was suggested by Yamaguchi that ^{41}Ca could be used in a similar fashion as ^{14}C to date calcium-containing samples with an age range of 100,000 to 1 million years [10,34]. In this section some possible uses of the long half-life of ^{41}Ca for dating are discussed.

Dating sea-bottom sediments

A promising application of radiocalcium dating is the ^{41}Ca dating of the shells of planktonic organisms, so-called foraminifera [35], which have been extensively studied using ^{14}C AMS techniques. A submarine sediment may be dated from the age of foraminifera. Presently, the date of a particular submarine deposit is often determined from relative dating to an ocean bed of known age. Absolute age measurements are preferred. In practice, the dating limit of the ^{14}C AMS is 500 to 50,000 years because of the relatively short half-life of ^{14}C . ^{41}Ca measurements would open the way to investigate very old foraminifera and to date sediments up to 1 million years old.

Because different species of foraminifera are found in different environments, paleontologists can use their fossils to determine past environments. If a sample of fossil

foraminifera contains many species that still exist today, the present-day distribution of those species can be used to infer the environment there when the fossils were alive. Even when samples contain all or mostly extinct species, data such as species diversity, the relative numbers of planktonic and benthic species (planktic:benthic ratio), and the ratios of different shell types are used to infer past environments.

In addition to using species distributions (whether directly or through diversity and other ratios) to study past environments, the chemistry of the shell can tell us a lot about the chemistry of the water in which it grew. Most importantly, the amount of ^{18}O in the ocean-water depends on the global temperature. During an ice age more water is stored on land in the form of ice, which is strongly depleted in ^{18}O . The fractionation in the uptake of the oxygen isotopes in the shell of the foraminifera is also temperature-dependent, and these effects together cause the temperature information to be stored in the deep-sea sediments. More ^{18}O in the shells indicates a colder earth climate.

Studies of stable oxygen isotopes in planktonic and benthic foram shells from hundreds of deep-sea cores worldwide have been used to map past water temperatures. These data help us understand how climate has changed in the past and thus how it may change in the future.

Dating of bones

The use of the a variety of dating methods [9] have resulted in the establishment of basic chronological structures for the hominid record in the early quaternary, especially for important sites in eastern Africa. For the late Quaternary - and in particular the last 30,000 to 50,000 years - chronological frameworks are also reasonably complete in broad outline for many areas of the world, largely because this period represents the current practical time span that can be dated by the ^{14}C method. In contrast, the dating frameworks for the period centered on the Middle Pleistocene, about 730,000 to 125,000 years ago, are generally imprecise and ambiguous. A radiocalcium dating method of bone material from this period could provide valuable information. The various dating methods and timescales are illustrated in figure 1.4.

The dating of bones using radiocalcium dating has been questioned in recent years. The $^{41}\text{Ca}/^{40}\text{Ca}$ ratio was thoroughly investigated in order to establish a dating method with ^{41}Ca [10, 36–39]. According to Wallner *et al* [33] it turned out that the natural $^{41}\text{Ca}/^{40}\text{Ca}$ isotope ratio shows remarkable fluctuations depending on the lithosphere-constitution, erosion rate, altitude and shielding of the cosmic radiation by the Earths geomagnetic field. Differences in the natural $^{41}\text{Ca}/\text{Ca}$ ratio of more than two orders of magnitude were observed, and a range of values from less than 10^{-15} up to a few times 10^{-14} was measured in samples collected at different regions around the world. The possibility to investigate the systematics of these differences is another motivation to improve the current and alternative methods for the detection of ^{41}Ca .

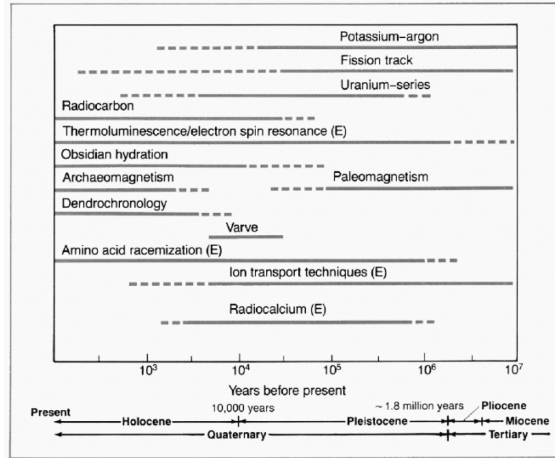


Figure 1.4: Various dating methods and the timescales on which they can be used. Adapted from Taylor [9]

1.2.5 Cosmochemistry

The ratio of $^{41}\text{Ca}/^{40}\text{Ca}$ can be used to determine the exposure history to thermal neutrons, since ^{41}Ca is produced by the capture of thermal neutrons into ^{40}Ca . Because the $^{41}\text{Ca}/^{40}\text{Ca}$ is being enriched by this process the detection limit for this application is less demanding. As an example, the ^{41}Ca in a drill core taken from an Apollo space-mission has been used to measure the low-energy neutron flux in the moon [40]. Other specific applications of ^{41}Ca measurements are [41, 42] the determination of terrestrial ages (preferably 30200 kyr) of meteorites and its use as a neutron flux monitor in the silicate phase of stony meteorites in order to obtain information about the shielding and size of the irradiated body. ^{41}Ca related exposure ages of meteorites can be employed in comparison with exposure ages related to other longer-lived cosmogenic nuclides to check the constancy of the galactic cosmic-ray flux with time. Furthermore, there is evidence for a connection between the flux of galactic cosmic rays and the Earth's climate during the past 200,000 years [43]. Further references on this topic are [16, 40, 44–50].

1.3 Experimental methods to detect ^{41}Ca

Different experimental methods exist for the detection of rare isotopes. The general challenge for the detection of an ultra-rare isotope such as ^{41}Ca are however the same. The following important issues have to be solved:

- **Isotope selectivity:** The signal of ^{41}Ca has to be separated from the signal of the main interfering isotope ^{40}Ca . The required isotope selectivity corresponds to the difference in abundance: fourteen orders of magnitude or more.

- **Efficiency:** In order to do a measurement of the $^{41}\text{Ca}/^{40}\text{Ca}$ in a reasonable time the efficiency of the experiment has to be high. The efficiency is defined here as the fraction of ^{41}Ca that can be detected from the amount originally available in the sample.
- **Detection sensitivity:** No matter how efficient the method is, starting with such a low abundance the final signal obtained from the ^{41}Ca present in the sample will never be very strong. Single atom (or ion) detection capability is therefore required.

In the next section the experimental approach used in this work, Atom Trap Trace Analysis (ATTA) is introduced. Before that however we introduce in this section three more established methods. Low-Level Counting (LLC) is conceptually the simplest method, and relies on the counting of the radiation emitted in the decay process. Accelerator Mass Spectrometry (AMS) is the most sensitive method for ^{41}Ca detection at the moment, but also requires the largest experimental setup. A much more compact technique is the recently developed method of Resonance Ionization Mass Spectrometry (RIMS), which is based on multi-step ionization using narrow-band diode lasers.

1.3.1 Low Level Counting

A well-known method to count the amount of unstable nuclei in a sample is Low Level Counting (LLC). In LLC the radiation emitted in the decay process of the specific nuclei of interest is counted. The sample and the detectors usually have to be shielded from the background due to cosmic radiation in order to achieve a high sensitivity. This method was first established for ^{14}C by de Vries in 1952 [51].

Can this method be applied to ^{41}Ca ? The decay of ^{41}Ca takes place by orbital electron capture directly to the ground state of ^{41}K [52]. Therefore, the only radiation given off is the low energy (3.3 keV) X-ray from the ^{41}K and a neutrino [9]. When measuring ^{41}Ca in a thick sample there is a problem of very strong self-absorption of these X-rays. This problem came up when analyzing concrete from nuclear reactors. In Japan concrete from decommissioned nuclear reactors has to be analyzed for ^{41}Ca activity. Above a maximum allowed activity of $1.5 \cdot 10^8$ Bq per ton of concrete a special barrier has to be constructed [53]. Therefore alternative methods to LLC like AMS and RIMS have been considered for determining the ^{41}Ca concentration.

Another problem is the long lifetime combined with the natural abundance of ^{41}Ca . The problems of counting the decay radiation using this method are pointed out by Raisbeck *et al* [10]: after estimating the natural abundance at $8 \cdot 10^{-15}$, it is mentioned that "This corresponds to an activity of $1 \cdot 10^{-3}$ disintegrations per minute per gramme of Ca - about 10^4 times smaller than for contemporary ^{14}C ." We have to conclude therefore that for the determination of natural ^{41}Ca concentrations LLC is likely to be not sensitive enough.

Fe, Ni and Ti by high-energy cosmic ray particles. This mechanism is the source of the production of ^{41}Ca in extraterrestrial materials like meteorites, and will be discussed in section 1.2.5.

The origin of ^{41}Ca on earth is capture of thermal neutrons by ^{40}Ca . The interaction of cosmic ray particles with the Earth's atmosphere produces a cascade of secondary particles, which is the main source of thermal neutrons on earth. Thermal neutrons are neutrons with a kinetic energy similar to the average kinetic energy of a room-temperature gas, which is around 10-100 meV.

The neutron-capture reaction is written as $^{40}\text{Ca}(n,\gamma)^{41}\text{Ca}$. Downward moving neutrons, produced by the interaction of cosmic rays with the upper atmosphere, are rapidly thermalized by the earth surface, giving rise to a significantly enhanced slow neutron flux at the air-surface interface [10]. Therefore ^{41}Ca is mainly produced at the earth's surface. For thermal neutrons the capture reaction on to ^{40}Ca has a fairly large cross-section of $\sigma = 0.41 \pm 0.02$ barn according to [11] and [12].

The decay of ^{41}Ca takes place by orbital electron capture directly into the nucleus, forming the ground state of ^{41}K under the emission of a neutrino. Therefore, the only detectable radiation resulting from the decay process is the low energy (3.3 keV) K α X-ray emission from the ^{41}K .

1.2.2 The lifetime and the abundance of ^{41}Ca

For a long time there has been uncertainty about the half-life and even about the existence of ^{41}Ca , as can be seen from figure 1.3. In the search for ^{41}Ca in the first half of the 20th century several authors have attempted to figure out the half-life of ^{41}Ca . The reported values are listed in table 1.2. The year 1951 was an important one in the history of ^{41}Ca research, as the value of the half-life changed from 'several months' in April [13] via $1.5 \cdot 10^4$ (reported as private communication by Brown *et al* [14]) to the very different value of $1.2 \pm 0.4 \cdot 10^5$ years reported [14] in October 1951. The presently accepted value is the mean of three measurements by Mabuchi *et al* [15], Klein *et al* [16] and Paul *et al* [17], and is given by Nishiizumi *et al* as $1.04 \pm 0.05 \cdot 10^5$ years [8].

The abundance of ^{41}Ca on earth can be estimated from the balance between the production and the decay rates. Raisbeck *et al* [10] calculate the concentration of ^{41}Ca after exposure to a flux (f) of neutrons for a time (t) as follows:

$$\frac{^{41}\text{Ca}}{^{40}\text{Ca}} = \frac{f\sigma t_{1/2}}{0.693} (1 - e^{-0.693t/t_{1/2}}) \quad (1.1)$$

Using a value of $3 \cdot 10^{-3} \text{ cm}^{-2}\text{s}^{-1}$ for the thermal flux [24], $\sigma = 440\text{mb}$ for the cross-section and $t \gg t_{1/2}$ ($t_{1/2} = 1.3 \cdot 10^5$ years from Emery *et al* [22]), Raisbeck *et al* get a saturation value of $^{41}\text{Ca}/^{40}\text{Ca} \sim 8 \cdot 10^{-15}$. In a recent measurement of the thermal neutron flux at sea-level [25] a value of $4 \text{ cm}^{-2}/\text{hr}$ was found: this corresponds to a flux of $1.1 \cdot 10^{-3} \text{ cm}^{-2}\text{s}^{-1}$, which would result in a saturation value which is a factor of 3 lower.

The first direct measurement of the natural concentration of ^{41}Ca was carried out in 1986 at the Argonne National Laboratory using the ATLAS linear accelerator system

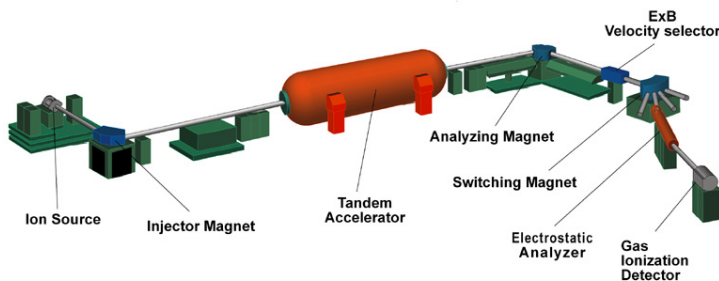


Figure 1.5: A schematic overview of a typical AMS facility [56]

1.3.2 Accelerator Mass Spectrometry

The most sensitive method for ^{41}Ca detection at the moment is Accelerator Mass Spectrometry (AMS) [54, 55]. A very low value of $(1.9 \pm 0.5) \cdot 10^{-15}$ for a $^{41}\text{Ca}/\text{Ca}$ ratio has been measured by Wallner *et al* [33] at the AMS laboratory in München. It should be noted however that only very few AMS machines can reach this sensitivity.

AMS combines techniques from magnetic spectrometry and nuclear physics. As an example, the schematic of the AMS instrument of PRIME Lab in the USA [56] is shown in figure 1.5. A beam of negative molecular and atomic ions is produced from the target material in the ion source and mass analyzed to approximately one atomic mass unit resolution. Ions are attracted to a solid foil or gas collision cell at high potential (110 MeV). As the ions pass through the foil or gas, two or more electrons are removed and the atomic and molecular ions become positively charged. The ions are then accelerated away from the positive potential. A relatively abundant charge state (e.g. $3+$ at 4 MeV for C) is selected by another mass analyzer. Removal of many of the electrons has destroyed all molecules. Only atomic ions at high energies (10 to 100 MeV) are left, which can be uniquely identified with an appropriate detector. The destruction of molecular isobars and unique identification of atomic isobars are the main reasons AMS has such a low detection limit. The size and complexity of these instruments can be rather daunting. The PRIME Lab AMS shown in figure 1.5 is approximately 60 m from one end to the other. Review articles describing recent AMS developments can be found in the references [6, 57, 58].

In the case of ^{14}C interfering isobars of ^{14}N are removed because they do not form negative ions: the interfering isobar for ^{41}Ca is ^{41}K , which however readily forms negative ions. Therefore molecular ions have to be used. The most efficient molecular ion to use is CaH_3^- from calcium hydride (CaH_2). CaH_3^- is much more easily formed than KH_3^- , therefore the ^{41}K background is strongly reduced. The drawback is the strong hygroscopic character of calcium hydride, which requires sample handling under argon atmosphere and an elaborate chemical treatment. However, in order to reach the high currents and the reduced background required in order to reach the sensitivity reported by Wallner *et al* [33] usage of calcium hydride can not be avoided. An important advan-

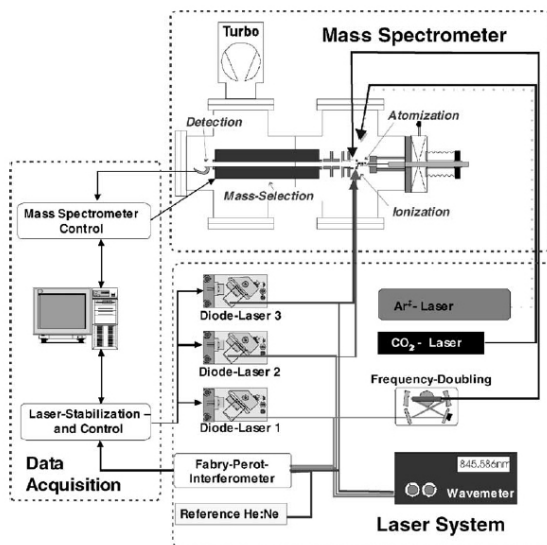


Figure 1.6: The experimental arrangement for high-resolution RIMS, taken from [62]

tage of ATTA when comparing to AMS might be the much simpler chemical preparation, especially attractive when considering medical applications which could take place in a dedicated room in an hospital.

1.3.3 Resonance Ionization Mass Spectrometry

In the field of rare isotope research, laser resonance ionization has nowadays become one of the key techniques [7]. The main isotope selective process is the multi-step ionization of the isotope of interest, followed by the detection of the ions using a quadrupole mass spectrometer. RIMS measurements with highest isotopic selectivity have been reported on a number of isotopes, like ^3He [59], ^{41}Ca [60], ^{90}Sr [18] and $^{135;137}\text{Cs}$ [61]. A high optical isotopic selectivity of $> 10^{12}$ has been realized in the case of ^{41}Ca , combined with an overall efficiency of $3 \cdot 10^{-5}$ [62]. As an example the experimental arrangement for high-resolution RIMS is shown in figure 1.6.

1.4 Atom Trap Trace Analysis

Atom Trap Trace Analysis (ATTA) is an experimental method pioneered in recent years by the group of Lu in Argonne, USA [63–67]. ATTA experiments combine various optical techniques, each of which is isotope selective. The mechanism of isotope selection is the repeated excitation (by a laser) of an optically accessible electronic transition in the neutral atom. Because of the isotope shift the scattering force induced by light of a fixed

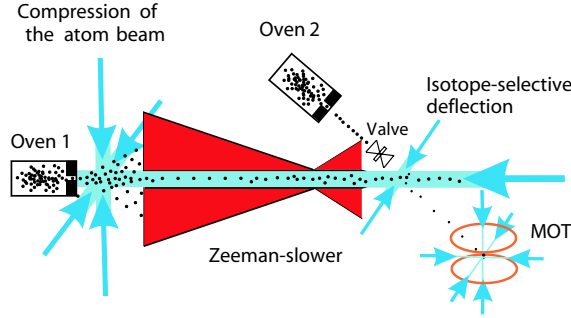


Figure 1.7: A schematic overview of the experimental setup, which will be presented in detail in chapter 3

Isotope	Applications	Trap transition	Reference
^{39}Ar	Trace deep ocean currents	$4s[3/2]_2 \rightarrow 4p[5/2]_3$, 812 nm	[4]
^{81}Kr	Dating of ancient groundwater	$5s[3/2]_2 \rightarrow 5p[5/2]_3$, 811 nm	[65]
^{90}Sr	Monitor nuclear fall out	$5^1S_0 \rightarrow 5^1P^o_1$, 461 nm	[69]
$^{135,137}\text{Cs}$	Monitor long-lived nuclear waste	$6^2S_{1/2} \rightarrow 6^2P_{3/2}$, 852 nm	[70]
^{205}Pb	Measure time-integrated solar neutrino flux	$6^3P_0 \rightarrow 7^3P^o_1$, 283 nm	[71, 72]

Table 1.3: Some isotopes that can be analyzed with ATTA. Sr, Cs, and Pb can be trapped in their ground levels

frequency is different for the different isotopes. It is the ratio between the natural linewidth and the isotope shift of the pumping transition that determines the selectivity that in principle can be reached between two neighboring isotopes. In the case of the calcium isotopes the isotope shift is about five times the natural linewidth; therefore isotope selectivity in laser pumping of calcium isotopes is possible. Reducing the Doppler broadening of the transition is a necessity. Therefore cold atoms are an ideal and necessary tool for ultra-sensitive isotope detection. Samples of cold atoms can be obtained by laser cooling and trapping in a magneto-optical trap (MOT) [68], which is the central element of an ATTA experiment. The trap is loaded by an atomic beam setup. To increase the fraction of atoms that can be captured by the trap a Zeeman slower is used. In the Zeeman slower part of the broad initial thermal distribution of atoms is slowed down to a velocity that can be captured by the trap, which is typically 50 m/s. A few examples of elements to which ATTA can be applied are given in table 1.4. To illustrate the method a schematic drawing of our experimental setup is shown in figure 1.7.

The final sensitivity that can be reached in an ATTA experiment is limited either by the background of ^{40}Ca atoms or by the loading rate of the trap. The background of ^{40}Ca atoms can be reduced by improving the isotope selectivity, the loading rate can be increased by improving the efficiency. In the ATTA measurements reported on in [66] the isotope selectivity was the limiting factor for the sensitivity. In this thesis the isotope selectivity has been investigated in detail. We will see that this results in a setup in which the search for ^{41}Ca atoms is no longer limited by the isotope selectivity but by the loading efficiency. At the moment the loading efficiency is limited by the laser power available for the experiment.

1.5 Outline of this thesis

In chapter 2 the necessary theory of laser cooling and trapping of calcium is treated. It will be shown how the spontaneous force that arises from the scattering of photons by an atom can be used to slow atoms down and even bring them to a halt in a magneto-optical trap. In chapter 3 the experimental setup is introduced that was designed and built during the course of this project. A number of computer simulations that have been done to study the feasibility of isotope separation using laser cooling and trapping is presented in chapter 4. These simulations have been an important tool for the design of various parts of the experimental setup and for the understanding of the experimental results. The experimental results that could be obtained with the constructed experiment are presented in chapter 5. The conclusions and a look into the future are presented in chapter 6.

